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ELSEVIER

Surface Science 382 (1997) L696–L699

surface science

Surface Science Letters

Second-harmonic generation spectroscopy and hyper-Rayleigh scattering in Langmuir–Blodgett films of fullerenes

E.D. Mishina ^{a,*}, A.A. Fedyanin ^a, D. Klimkin ^a, A.A. Nikulin ^a, O.A. Aktsipetrov ^a,
S.L. Vorob'eva ^b, V.R. Novak ^b, M.A.C. Devillers ^c, Th. Rasing ^c

^a *Department of Physics, Moscow State University, Moscow 119899, Russia*

^b *Institute of Physical Problems, Zelenograd, Russia*

^c *Research Institute for Materials, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands*

Received 9 October 1996; accepted for publication 28 February 1997

Abstract

Optical second-harmonic generation (SHG) spectroscopy and hyper-Rayleigh scattering (HRS) were studied in thin Langmuir–Blodgett films of fullerenes. For films above five monolayers a coherent SHG signal was observed, whereas a one-monolayer film only produced HRS. The HRS indicatrices were measured, and a correlation length of the non-linear polarization of about 100 nm was obtained.

The increase in SHG intensity for C₆₀-CN films in comparison with that of C₆₀ films is well pronounced, particularly at the blue end of the SHG spectra, and is attributed to a resonant surface electric-dipole contribution. © 1997 Elsevier Science B.V.

Keywords: Fullerenes; Second harmonic generation; Surface structure

Optical second-harmonic generation (SHG) has been shown to be a sensitive probe of the electronic properties, structural symmetry and morphology of surfaces, interfaces and very thin films (down to a thickness of monolayers) such as Langmuir–Blodgett (LB) films [1]. Homogeneous, smooth, linear films produce coherent (specular) SHG. The characteristics of coherent SHG radiation (wave polarization, azimuthal anisotropy and dependence on angle of incidence) depend on the non-linear susceptibility tensor components of the film, and reflect the electronic and symmetry properties of the film. Inhomogeneous structures pro-

duce incoherent SHG which is diffuse and depolarized, and can be considered as a limiting case of hyper-Rayleigh scattering (HRS). HRS is mostly studied in the bulk of isotropic media such as solutions or suspensions in order to measure the non-linear polarizability of a single scatterer. These two types of SHG are usually studied separately, as most structures do not show both coherent and incoherent SHG.

However, it was shown recently that inhomogeneous ferroelectric thin films generate both coherent and incoherent SHG [2]. In particular, the presence of $s_{in} - s_{out}$ SHG, which is symmetry-forbidden for homogeneous surfaces, can be a sensitive probe for studying the microstructure of a surface [3,4]. Therefore a combination of two measure-

* Corresponding author: Fax: +7 95 9393113;
e-mail: mishina@astra.phys.msu.su

ments is required, i.e. the coherent SHG signal in the specular direction and the incoherent diffuse signal which is due to HRS. Measurements of HRS indicatrices in thin films allow us to obtain the correlation length of the non-linear sources and yield an estimate of how homogeneous they are. Therefore, HRS can also be a sensitive probe for studying the quality and homogeneity of LB films.

The special features of C_{60} molecules have attracted great interest since their discovery, including several (coherent) SHG studies [5–9]. In the present paper we report the results of SHG and HRS experiments on thin Langmuir–Blodgett films of fullerenes. We show here that the nature of SHG for thick films differs from that for very thin films, and demonstrate the transformation from coherent SHG to incoherent HRS with decreasing film thickness. Modification of the C_{60} molecules to C_{60} -CN leads to an enhanced SHG response but a reduced HRS response.

The synthesis of the C_{60} -tetracyanoethylene oxide derivative (C_{60} -CN) will be described elsewhere [10]. C_{60} and C_{60} -CN films were formed on a water surface and then deposited onto fused quartz substrates by the Langmuir–Schaefer method. The area per molecule was about 30 \AA^2 . Pressure–area curves indicated that C_{60} molecules formed clusters of about 100 molecules on the water surface, with an average diameter of about 5.5 nm. These clusters are not destroyed during deposition on a substrate.

We studied LB monolayers and multilayers (5, 10 and 15 layers). The thickness of the films was measured by an interference microscope (Interfac Carl Zeiss). The thickness of LB C_{60} monolayers was found to be $2.9 \pm 0.1 \text{ nm}$, and that of C_{60} -CN was $2.5 \pm 0.1 \text{ nm}$. As the diameter of C_{60} molecules is equal to 7.1 \AA [5], the thickness of LB monolayers is close to three molecular diameters.

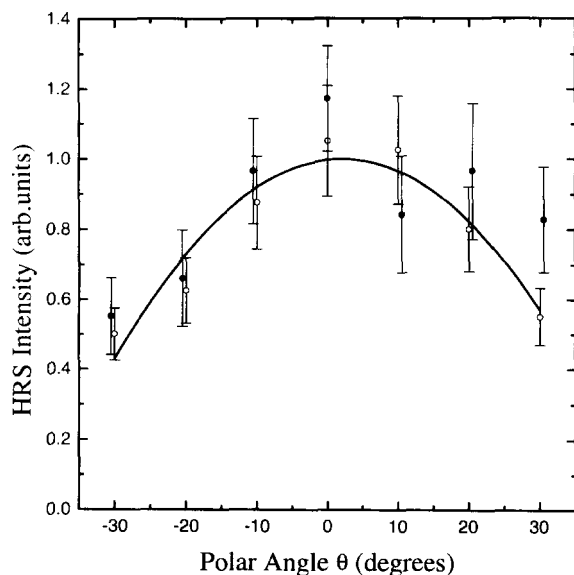
For the SHG experiments the output of a Ti:sapphire laser in the range 710–800 nm was used with a pulse width of about 100 fs, a repetition rate of 82 MHz, and an average power of 100 mW focused onto a spot of about $100 \text{ }\mu\text{m}$ diameter at a 45° angle of incidence. Both fundamental and SHG waves were p - or s -polarized (p – p and s – s

polarization combinations, respectively). For measurement of the HRS scattering indicatrix, the diffuse SHG intensity was integrated over a $2 \times 10^{-3} \text{ sr}$ solid angle which was determined by the angular resolution of the detector. Spectral studies showed that the signal was due to SHG, and no two-photon luminescence was found. No laser-induced changes of the C_{60} films were observed, and the quadratic law for SHG intensity versus fundamental power was fulfilled perfectly. The azimuthal dependence of the SHG intensity was found to be isotropic, and the signal strength was at least five times larger than that from the quartz substrate.

Absorption spectra were measured in the UV and visible range (200–700 nm) with the use of an LO MO CSVU-23 spectrophotometer.

The measurements of SHG intensity as a function of polar angle show a dramatic difference in the SHG angular distribution for fullerene LB monolayers and multilayers. For multilayers in the s – s polarization combination, the signal is absent for all values of the polar angle. For monolayers, the SHG is generated for both p – p and s – s polarization combinations, and is diffuse and slightly polarized. No pronounced peak in the specular direction was observed (Fig. 1). The diffuse SHG for monolayers is more than one order of magnitude lower than the specular signal for multilayers. Normalized scattering indicatrices for C_{60} and C_{60} -CN LB monolayers are coincident with each other within the error bar (see Fig. 1). However, the absolute value of the diffuse SHG signal for C_{60} was about a factor of five higher than for the C_{60} -CN case.

It was mentioned in Ref. [7] that for small thicknesses, a strong deviation from the theoretical thickness dependence of the SHG intensity from C_{60} films was observed. Only “allowed” polarization combinations were studied in Ref. [7], and the observed deviations were explained by surface roughness (as for rough surfaces the difference between p - and s -polarization diminishes). For the evaporated films studied in Ref. [7], clusters of C_{60} molecules of several nm in diameter were well distinguished even on the surface of 800 nm thick films, and pronounced deviations from the calculated dependence of the SHG intensity as a func-



$$l_{\text{corr}} = 100 \text{ nm}$$

Fig. 1. HRS indicatrices for C_{60} (open dots) and $\text{C}_{60}\text{-CN}$ (filled dots) LB monolayers in the s - s polarization combination. A polar angle of zero corresponds to the specular direction.

tion of film thickness were observed up to 500 nm. In our experiments, much thinner films obtained by the LB technique appear to be quite homogeneous, as no forbidden SHG in the s - s polarization combination was observed.

The scattering indicatrix for the diffuse component of the SHG radiation is determined by the correlation function of the spatial fluctuations of the randomly distributed non-linear polarization. One can easily imagine various probable sources of these fluctuations, such as random orientations of the polarization of single molecules or single clusters of C_{60} molecules, random values of the polarization of a single cluster (for instance through the fluctuations of the number of C_{60} molecules in a cluster), thickness fluctuations, etc.

Using a formalism analogous to that described in Ref. [2] we obtained l_{corr} to be about 100 nm. This means that for LB monolayers of fullerenes, the C_{60} clusters deposited on the substrate show some correlation between them, on a scale which is about ten times their size. However, thicker films appear to be perfectly homogeneous.

Multilayer films produce a strong specular SHG which shows all the properties of coherent SHG: it is polarized according to the symmetry rules for isotropic media (no signal for the s - s polarization combination was observed) and propagates within a narrow solid angle. The specular signal of coherent SHG from thick films was at least two orders of magnitude larger than the HRS intensity for monolayers, integrated over the detector aperture in the specular direction. This means that the total integrated HRS intensity of πsr is of the same order of magnitude as the specular signal from thick films.

The SHG spectra for C_{60} and $\text{C}_{60}\text{-CN}$ films with a thickness of 10 Langmuir layers are shown in Fig. 2. They have a strong wavelength dependence in the SHG range of 350–400 nm. The SHG intensity is enhanced by a factor of 5 for $\text{C}_{60}\text{-CN}$ films in comparison to C_{60} . At the same time, the absorption spectra for C_{60} and $\text{C}_{60}\text{-CN}$ films are practically identical to each other. Since the SHG spectra were obtained in a rather limited wavelength range, only the edge of a resonance band is observed. Nevertheless, a higher non-linear suscep-

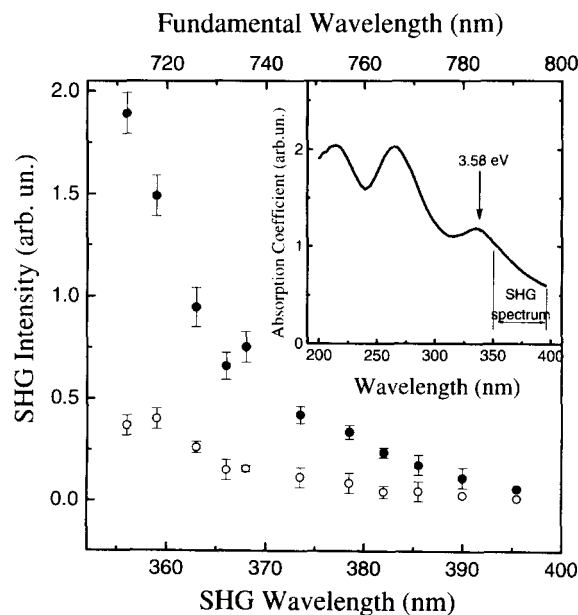


Fig. 2. SHG excitation spectrum for ten-layer films (open circles correspond to C_{60} , filled circles to $\text{C}_{60}\text{-CN}$). Insert: linear absorption spectrum for the $\text{C}_{60}\text{-CN}$ film.

tibility due to a molecular modification is clearly demonstrated.

Individual C_{60} molecules are centrosymmetric and therefore do not produce electric-dipole SHG, but electric-quadrupole as well as magneto-dipole SHG is allowed. In the range of fundamental frequencies available in our experiment, C_{60} molecules have a magneto-dipole transition at 1.81 eV (685 nm) [5]. In the SH range, there is an electric-dipole transition at 3.58 eV (346 nm). The latter is well pronounced in absorption spectra. Therefore the SHG spectra are very close to double resonant conditions for both the fundamental and SHG frequencies at the blue edge of our measurements.

C_{60} -CN molecules have no inversion symmetry. Therefore the electric dipole transition at 3.58 eV becomes allowed, giving rise to a strong resonance of the hyperpolarizability at 3.58 eV. The change of symmetry can also influence the value of the magnetic-dipole hyperpolarizability at 1.81 eV, but one would expect this to be a minor effect.

On a macroscopic level, both C_{60} and C_{60} -CN films are centrosymmetric: electric-dipole SHG is forbidden in the bulk of the film, and only magnetic-dipole and quadrupole SHG can be generated. At the symmetry-breaking interfaces (air/film and film/substrate) electric-dipole allowed terms should be taken into account. It was shown in Ref. [7], however, that for C_{60} films at double resonant conditions the main contribution to SHG is still coming from the bulk of the film, whereas far from resonance the bulk contribution decreases down to the interface contributions. On the other hand, the surface layer of the C_{60} -CN films is expected to form a more or less ordered structure. This will lead to a strong electric-dipole surface contribution to the SHG, which is why the SHG response of the C_{60} -CN films is so much stronger than that for C_{60} films.

Two types of SHG were observed in fullerene LB films: HRS for monolayers and coherent SHG for thicker films. For monolayers, the HRS indicatrices were measured and a correlation length of the nonlinear polarization was calculated, which

turned out to be about 100 nm. The SHG spectra for fullerene multilayers were studied. The increase of SHG intensity for C_{60} -CN films in comparison to C_{60} films is well pronounced, particularly at the blue end of the SHG spectra, and is attributed to a surface electric-dipole resonant contribution. In future experiments we plan to investigate the transition from HRS to coherent SHG in the intermediate thickness range (1–5 ML).

Acknowledgements

This work was supported by the Russian Ministry of Science (Program “Fullerenes and small clusters”). One of us (E.D.M.) would like to thank the Research Institute for Materials of the University of Nijmegen for their hospitality and financial support.

References

- [1] G.J. Ashwell, P.D. Jackson, G. Jefferies, I.R. Gentle, C.H.L. Kennard, *J. Mater. Chem.* 6 (1996) 137.
- [2] O.A. Aktsipetrov, A.A. Fedyanin, D.A. Klimkin, A.A. Nikulin, E.D. Mishina, A.S. Sigov, K.A. Vorotilov, C.W. van Hasselt, M.A.C. Devillers, Th. Rasing, *Ferroelectrics* 186 (1996) 215.
- [3] O.A. Aktsipetrov, I.M. Baranova, Yu.A. Ilinskii, *Sov. Phys. JETP* 64 (1986) 167.
- [4] O.A. Aktsipetrov, N.N. Akhmediev, I.M. Baranova, E.D. Mishina, V.R. Novak, *Sov. Phys. JETP* 62 (1985) 524.
- [5] B. Koopmans, A.M. Janner, H.T. Jonkman, G.A. Sawatzky, F. van der Woude, *Phys. Rev. Lett.* 71 (1993) 3569.
- [6] B. Koopmans, A. Anema, H.T. Jonkman, G.A. Sawatzky, F. van der Woude, *Phys. Rev. B* 48 (1993) 2759.
- [7] D. Wilk, D. Johansmann, C. Stanners, Y.R. Shen, *Phys. Rev. B* 51 (1995) 10057.
- [8] X.K. Wang, T.G. Zhang, W.P. Lin, S.Z. Liu, G.K. Wong, M.M. Kappes, R.P.H. Chang, J.B. Ketterson, *Appl. Phys. Lett.* 60 (1992) 810.
- [9] O.A. Aktsipetrov, O. Keller, K. Pedersen, A.A. Nikulin, N.N. Novikova, A.A. Fedyanin, *Phys. Lett. A* 179 (1993) 149.
- [10] V.R. Novak, S.L. Vorob'eva, I.V. Myagkov, *Mol. Mater.* 7 (1996) 175.